SYNTHESIS AND APPLICATIONS OF DEEP EUTECTIC SOLVENTS IN VALORIZATION OF BIOMASS DERIVATIVES

Synopsis of the Ph.D. Thesis

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1. ABSTRACT

Biomass valorization has emerged as an important avenue for the synthesis of chemicals and fuels. Biomass can be transformed into valuable chemicals through various reactions, e.g., hydrolysis, esterification, condensation, dehydration, etc. It is imperative to design suitable catalytic systems to obtain the maximum yield of desired chemicals. The deficiencies of homogeneous and heterogeneous catalysts currently used in transformation have forced researchers to search for better alternatives. Deep eutectic solvents (DES) are a type of ionic liquids that are formed by proportional mixing of hydrogen bond donors and hydrogen bond acceptors. They have melting points lower than that of individual constituents. DES can be used as a catalyst and a solvent in biomass transformations. The current work comprises four schemes for the synthesis of valuable chemicals from biomass-derived chemicals using some novel DES as catalysts in reactions. In the first scheme, eugenol was converted into eugenol benzoate through esterification using acidic DES. The catalyst was synthesized from choline chloride as HBA and carboxylic acids as HBDs and gave optimum eugenol conversion of 90.42% when catalyst Chcl-4-p-TSA was used. In the second scheme, a novel magnetically separable DES was synthesized (choline chloride as HBA, carboxylic acid as HBD, ferric chloride as magnetic component) and used in the transformation of furfuryl alcohol (FAL) into butyl levulinate (BL). This is the first research work in which magnetic DES was used as a catalyst for FAL alcoholysis. The highest BL yield of 98.42 was obtained with p-TSAM-based MDES. In the third scheme, CTAB-based hydrophobic DES was used as a catalyst in the synthesis of BL from levulinic acid. The highest conversion of 88.77% was obtained with the catalyst CTAB-3-p-TSAM.In the last scheme, basic DES (potassium carbonate as salt and ethylene glycol as HBD) was used in aldol condensation of furfural with acetone. The catalyst K_2CO_3: EG (1:6) gave 89.47% furfural conversion. This is the first instance in which a basic DES is used as a catalyst successfully in aldol condensation. Overall, the research work successfully proves that DES can be used as catalysts in biomass transformation reactions. DES will become more commonplace catalysts in biomass conversions as their tunable nature makes them useful in numerous industrial applications.

2. INTRODUCTION

2.1 Biomass as a source of valuable chemicals

Demand for energy and chemicals is causing rapid depletion of crude oil and natural gas reserves. Burning fossil fuels is also contributing to global warming and climate change. Crude oil, natural gas, and coal serve as raw material feedstock for chemical industries. Although chemical industries play a vital role in driving modern civilization, their dependence on fossil resources and contribution to environmental pollution attracts negative attention[1]. To achieve social, health, and ecological benefits, tremendous efforts have been expended to transform traditional chemical manufacturing processes into more sustainable ones. Sustainable chemical production can be achieved by recycling waste, using efficient pollution control techniques, and using biomass as raw material [2]. Biomass is an abundant, renewable, carbon-neutral material that can replace fossil-based raw materials. Using biomass will reduce environmental impact due to low pollution, less CO_2 contribution to the atmosphere, and more biodegradable and sustainable products[3]. Plant-derived biomass is composed of mainly cellulose (40–50%), hemicellulose (25–30%), and lignin (15–20%). Biomass can also contain proteins, fats, waxes, organic acids, minerals, and free sugars as their structural or metabolic components. Cellulose is a linear homogenous polymer of 7000 to 15000 glucose units linked by β-1-4 glycosidic linkages. Hemicellulose is a branched or linear heteropolymer of 200–400 units of different pentoses (C_5 sugars: xylose, arabinose), hexoses (C_6 sugars: mannose, glucose, galactose), and uronic acids with an amorphous structure. Lignin is an amorphous cross-linked polymer of the three phenyl propane units p-coumaryl, coniferyl and sinapyl alcohol.

The US Department of Energy has identified 12 platform chemicals that could substitute fossil fuel-derived products. In 2010, following chemicals were added:1,4-dicarboxylic acids (succinic, fumaric and malic acid), 2,5-furan dicarboxylic acid,3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol/arabinitol[4]. The biomass feedstock is pretreated by either of 3 methods: Physical, chemical, biological, or combination. Pretreated biomass is subjected to chemical or biological conversion processes. Platform chemicals produced could be converted into value added derivatives. The structure of the targeted molecule decides the selection of renewable raw material for valorization [2]. Cellulose and hemicellulose fraction of biomass can be converted into hexose and pentose sugars via hydrolysis. The monosaccharides (glucose, xylose, arabinose) can be

converted into ethanol, furfural, lactic acid, levulinic acid, sorbitol, mannitol, and glycerol. Chemical conversion of these primary products produces alcohols, diols, carboxylic acids, organic acids, polymers, furfural, bio-gas, liquid alkanes, and phenol. These products find applications in numerous industries, such as food, pharmaceuticals, biomedical products, agrochemicals, aerospace, the building sector, filler materials, fragrances, food, cosmetics, etc. [5].

2.2 Catalysts used in biomass valorization

The transformation of biomass is carried out through numerous chemical reactions. Chemical reactions include hydrolysis, esterification, transesterification, dehydration, isomerization, hydrogenation, oxidation, polymerization, etherification, aldol condensation, dimerization, hydrodeoxygenation, etc. The conversion and yield of these reactions depend on the types of catalyst used. Better catalyst design is needed to make biomass conversions as efficient as petrochemical industries. The catalyst should have desirable properties, i.e., cheaper, high selectivity, better hydrothermal and mechanical stabilities, easy separation, simple synthesis methods, high surface area, better activity, and high turnover frequency. The catalyst should function properly under mild process conditions requiring easier reactor configurations. The following catalysts were used in biomass conversion reactions and were reported in the literature: Bulk Metal Oxides, Metal-Oxide-Supported Metals, Acid-Functionalized Mesoporous Materials, Ion-Exchanged Resins, Zeolites and Zeolite-Supported Metals, Carbonaceous materials, Ionic Liquids[6].

2.3 An exploration of using deep eutectic solvents as catalysts in biomass valorization

DESs, a subset of ionic liquids, consist of binary or ternary eutectic blends of hydrogen bond donors (HBD) and acceptors (HBA). These mixtures possess melting points below those of individual components, remaining in a liquid state up to 70°C. Common HBDs include Lewis or Brønsted acids, while HBAs typically comprise quaternary ammonium halides or other anions. DES is usually liquid at near-eutectic or near-eutectic composition. Varying ratios of Lewis or Brønsted acids and bases control acidity/alkalinity. Distinguishing themselves from conventional ionic liquids, DESs exhibit a broader range of anions and cations in their structure, coupled with the biodegradable nature of their constituents. DESs offer numerous advantages, including low vapor pressures, excellent thermal stability, ease of recycling, low toxicity, biodegradability, high solubility, and tailorable. DES is utilized in various applications, such as solvents and catalysts, e.g., metallurgy, gas separations, biocatalysis, genomics, etc.

DESs are being researched for their catalytic applications in biomass valorization. They offer the advantages of both homogenous and heterogeneous catalysts. They are suitable solvents that can convert a heterogeneous system into a homogeneous one. The catalytic DESs can be categorized as Lewis acid-type or Brønsted acid-type DESs. The Lewis acid-type DESs contain chlorides of transition metals such as Zn, Fe, and Cr combined with mainly choline chloride (ChCl). These DES were used for transesterification, lignin fractionation, cellulose conversion to gluconic acid, etc. Brønsted acid-type DESs mostly contain ChCl combined with organic acids such as oxalic acid, citric acid, acetic acid, malonic acid, formic acid, p-toluene sulfonic acid (p-TSA), or alcohols such as ethylene glycol or glycerol or amides such as urea. These DES were used for the degradation of alkali lignin, change of corncob to furfuryl alcohol, epoxidation, etc. As DES are tunable, their properties can be configured for particular reactions[7].

2.4 Research Gaps

From the literature survey, we found that DES was not used as catalysts in the synthesis of eugenol benzoate from eugenol, the synthesis of butyl levulinate from levulinic acid, alcoholysis of furfuryl alcohol to butyl levulinate, and aldol condensation of furfural.

The aims of this project are:

To explore applications of DES as catalysts in various biomass transformation reactions such as esterification, alcoholysis, and aldol condensation.

We plan to use DES as a catalyst in

1. Synthesis of eugenol benzoate from eugenol and benzoic acid
2. Alcoholysis of furfuryl alcohol to butyl levulinate
3. Esterification of Levulinic acid to butyl levulinate
4. Aldol Condensation of furfural and acetone

3. AIM & OBJECTIVES:

Based on the research gap, the following four schemes are proposed to explore the applicability of DES in the valorization of biomass to value-added products.

Scheme I: Esterification of Eugenol to Eugenol Benzoate by using acidic DES as a catalyst

Catalyst: Choline chloride-based DES with various carboxylic acids (acetic acid, oxalic acid, p-TSA, tartaric acid, citric acid) as HBD.

Scheme II: Alcoholysis of furfuryl alcohol to Butyl levulinate by using magnetic DES as a catalyst

Catalyst: Magnetic deep eutectic solvents (MDES) with choline chloride as HBA and various carboxylic acids (citric, oxalic acid, p-TSAM) as HBD.

Scheme III: Esterification of Levulinic acid (LA) to Butyl levulinate by using CTAB-based DES

Catalyst: CTAB-carboxylic acid-based hydrophobic DES with CTAB as HBA and carboxylic acids (citric, oxalic, p-TSAM) as HBD.

Scheme IV: Aldol Condensation of the furfural with acetone by using basic DES as a catalyst

Catalyst: Basic DES was formed from potassium carbonate as salt and ethylene glycol as HBD

Each scheme has the following objectives involved:

1) Synthesis of the DESs and their screening in the reaction
2) Detailed characterization to understand the structure and correlation with activity (acidity/alkalinity, NMR, FTIR)
3) Optimization of reaction parameters (reaction temperature, reaction time, mole ratio, catalyst loading)

Overall, these schemes will be helpful in demonstrating the broad application of DESs as the catalyst in biomass valorization. The developed schemes and catalysts will be beneficial for converting biomass into value-added products, paving the way for scalable, eco-friendly industrial processes and future advancements in green chemistry applications.

4. LITERATURE REVIEW

4.1 Scheme I: Esterification of Eugenol to Eugenol Benzoate by using acidic DES as a catalyst

Eugenol ($C_{10}H_{12}0_2$;4-allyl-2-methoxyphenol) is an important component of clove essential oil obtained from the Syzygium aromaticum plant flower buds. It exhibits antioxidant, analgesic, anti-anaphylactic, anesthetic, anticonvulsant, and anti-inflammatory properties. It also displays antibacterial, antifungal, and antiviral activities. It's being explored as an anticancer medicine. It is used in food and cosmetic products as a flavoring agent. It is used in dentistry as a topical antiseptic and in dental preparations. Eugenol could be toxic at higher doses due to the formation of phenoxyl radicals and quinine intermediates. Adverse effects of Eugenol include allergic reactions, contact dermatitis, and inflammation. Very high concentrations might lead to liver failure[8]. Esterification of Eugenol to eugenol benzoate could mitigate its allergic and toxic effects. The addition of the benzoate group to the hydroxyl group reduced antioxidant activities but increased its biological activity. Eugenol benzoate exhibited improved antimicrobial and lipophilic activities than Eugenol[9].

Benzoyl chloride was used as a catalyst, but these catalysts were challenging to separate from the reaction mixture and were toxic to the environment. Heterogeneous catalysts such as waste kaolin, Amberlyst A-21, and mesoporous super acid zirconia-based catalysts were reported in the literature. Low yields, high reaction times, and complex synthesis of catalysts were drawbacks of these catalysts[9,10]. Horchani *et al*. used an enzyme catalyst, but the ester yield was low, and a higher reaction time was required. There was also the possibility of enzyme catalysts denatured if reaction conditions were slightly changed[11]. Homogeneous mineral acid catalysts are effective but prove to be detrimental to the environment due to incomplete separation from the reaction mixture and corrosion. Heterogeneous acid catalysts are environmentally benign and easy to separate from the reaction mixture. However, they do suffer from mass transfer limitations. The development of suitable catalysts to increase the yield of esterification has been a significant focus of researchers. A prior literature survey revealed the following information on the use of DES as a catalyst in esterification. Alhassan *et al*. demonstrated an 86.62% conversion in the esterification of waste tire pyrolysis oil using ChCl-p-TSA DES (1:4). Taysun *et al.* achieved an 85.0% conversion in the synthesis of acetic acid esters by employing benzyl tri-methyl ammonium chloride (BTMAC)-p-TSA DES under optimal conditions. Yu Ri Lee *et al*. utilized a DES

composed of tetrabutyl ammonium chloride and acetic acid (1:2) to synthesize esters from palmitic acid and methanol, achieving the highest yield of 94.3%[12].

Synthesis of eugenol benzoate by esterification of eugenol by using DES as a catalyst has never been studied. Our research focuses on synthesizing acidic DES by using choline chloride as HBA and carboxylic acids as HBD and using them in eugenol esterification with benzoic acid. Acidic DESs were prepared using various carboxylic acids and choline chloride, as described by Abbott. Para-toluenesulfonic acid-choline chloride DES was prepared by the method described by Assanosi et al. The acidity of deep eutectic solvents was determined by the process described in literature .[13,14]

4.2 Scheme II: Alcoholysis of furfuryl alcohol to Butyl levulinate by using magnetic DES as catalyst

Butyl levulinate finds applications as component of fuel blends, as fragrances, as flavoring agent, as plasticizers, polymer precursors and as solvent. Hydrolysis of hemicellulose and dehydration of xylose produces furfural. Hydrogenation of furfural produces furfuryl alcohol. Butyl levulinate can be synthesized from furfuryl alcohol by acid-catalyzed alcoholysis. Production of levulinic acid involves loss of one carbon so using levulinic acid does not provide good atom economy. Conversion of FAL to butyl levulinate exhibits good atom economy and easy product separation. Furfuryl alcohol is cheaper and highly reactive. So, the manufacture of BL from furfuryl alcohol is economical, faster, and greener. The selection of catalysts is an important aspect that affects the furfuryl alcohol conversion and butyl levulinate yield[15].FAL alcoholysis was always carried out at lower FAL concentration as furfuryl alcohol polymerizes at higher concentration in presence of strong catalysts. FAL polymerization was also favored at higher temperatures. For FAL alcoholysis reaction, the conversion of FAL and yield of BL were strongly correlated the Brønsted acid site density. Although, Lewis acid sites could also play important role[16].

Following catalysts have been used for alcoholysis of furfuryl alcohol to BL: homogeneous mineral acids ,metal salts, metal oxides, 5-sulfosalicylic acid ,phosphomolybdic acid supported on activated charcoal, modified clays, zeolites, lignosulfonate-based carbonaceous solid acid, sulfonated carbon, graphene oxide, reduced graphite oxide, sulfonic acid-grafted silica gel, propylsulfonic acid-functionalized SBA-15, sulfonated titanium nanotubes, acid functionalized

polymer-coated carbon nanotubes, acidic ion exchange resins, metal triflates, modified TPA, metal-organic frameworks, and Bronsted ionic liquids[17].

Heterogeneous acid catalysts proved to be better in the alcoholysis of FAL due to low corrosion and ease of separation from the reaction mixture for regeneration. Separation of heterogeneous catalysts from the reaction mixture was easier. Difficult synthesis, diffusional resistance during reaction, and high costs negate this advantage. Some of these catalysts suffer from catalyst deactivation due to the deposition of humins. The butanolysis reaction between furfuryl alcohol and n-butanol is plagued by problems: formation of humins, low molar ratio of FAL to n-butanol, harsh reaction conditions, long reaction times, complex methods of catalyst recovery and regeneration.

So far, no examples of using DES as a catalyst were found in the literature for the synthesis of BL from FAL. Current research focuses on developing a suitable catalyst to overcome the above-mentioned problems. We have synthesized and tested magnetic deep eutectic solvents as catalysts for the formation of n-butyl levulinate from the alcoholysis of furfuryl alcohol. Synthesis of magnetic DES was performed by following the method described in literature with small modification in synthesis process.

4.3. Scheme III-Esterification of Levulinic acid (LA) to Butyl levulinate by using CTAB based DES

Butyl levulinate can be synthesized by esterification reaction between LA and n-butanol. LA can react with n-butanol in absence of catalysts but the reaction rate is low. To increase rate of reaction, high temperature or catalysts or both must be used. Apart from reaction parameters, selecting appropriate catalyst is essential to improve BL yield. Total surface acidity and Brønsted acidity of the catalyst were major factors in the conversion. Structure, texture, porosity, surface area can influence activity and selectivity of catalyst. The rate of esterification is linearly dependent on the diffusion rate of the reactants which in turn affects accessibility to active sites of catalyst. The rate of diffusion of reagents to active sites is controlled by surface area and pore size of heterogeneous catalysts. The molecular weight of alcohol also affects diffusion rate. So, designing catalyst with proper surface area and porosity can reduce diffusional resistance and can improve LA conversion and BL yield. For heterogeneous catalysis, catalyst morphology and

reactor configuration influences heat and mass transfer effects. These, in turn, control reaction rate[18,19].

Esterification of LA with n-butyl levulinate has been carried out by using various catalysts such as homogenous acids and heterogeneous solid acids. Due to the disadvantages of using mineral acids as catalysts, heterogeneous acids are being promoted to replace homogeneous catalytic systems for the esterification of levulinic acid. Heterogeneous solid acids reported for esterification of levulinic acid to butyl levulinate are: metal salts, metal oxides, zeolites, Zr-containing MOFs , functionalized silica, sulfonated carbon, acidic ion-exchange resins, heteropolyacids, sulfonated titanium dioxide nanotubes, halloysite clay etc.[19–21].Owing to complex synthesis, deactivation, and difficulty in regeneration, many of these heterogeneous catalysts were deemed impractical for industrial applications. Various side reactions were observed, such as dehydration of alcohol in the presence of an acid catalyst to give dibutyl ether or butene. The application of CTAB-based DES in the synthesis of BL from LA has still not been explored. To overcome these shortfalls of existing catalysts, we have tested CTAB-based hydrophobic deep eutectic solvents as catalysts for the preparation of butyl levulinate from levulinic acid. The procedure Kun Li et al. reported was used to synthesize HDEs[22].

4.4. Scheme IV: Aldol Condensation of the furfural with acetone by using basic DES as a catalyst

Furfural can be obtained from xylose, which is obtained from hydrolysis of hemicellulose fraction biomass. In aldol condensation, aldehydes and ketones can react to form high MW products, which have more economic value. Furfural is reacted with biomass-derived acetone by aldol condensation to produce C_8 and C_{13} adducts. These adducts can be transformed by hydrogenation and deep hydrodeoxygenation into high-quality diesel fuels[23]. Aldol condensation can be carried out in the presence of basic and acidic catalysts. Alkalis such as KOH and NaOH were effective but were challenging to separate from reaction mixture, require vast amounts of water to neutralize, corrosive and toxic. The alkalis tend to react with atmospheric CO_2 to form carbonates, thus reducing their efficiency. Many heterogeneous metal oxide catalysts were reported, for example MgO–ZrO_2, alkali and alkaline earth oxides, alkali-exchanged zeolites, MCM41, aluminophosphate oxynitrides, ion-exchange resins, and activated Mg-Al hydrotalcite, phosphates, etc. These catalysts needed complex preparation, gave low conversion, required high

reaction times, and were deactivated due to poisoning[24]. The use of basic DES as a catalyst for aldol condensation of furfural with acetone is not carried out as per the literature, and hence, to overcome these drawbacks, we propose to use potassium carbonate and ethylene glycol-based basic deep eutectic solvent as catalysts. The catalysts were assessed for their activity, reaction conditions were optimized for maximum conversion, and catalyst recycle was studied.

5. CONTRIBUTION

5.1 Scheme I: Esterification of Eugenol to Eugenol Benzoate by using acidic DES as a catalyst

Results and discussion:

5.1.1 Acidity of deep eutectic solvents

The acidity of deep eutectic solvents is given in Table 5.1.1. The acidity of DES is affected by the nature and type of HBD. Apart from the acidic nature, the ratio of HBD/HBA in DES also affects the acidity of DES. Increasing the amount of p-TSA increased the acidity of prepared DES. Catalyst ChCl-p-TSA DES-4 (molar ratio - 1:4) displayed the highest acidity, as p-TSA is a strong acid.

Table 5.1.1: Acidity of DES

Name of DES	Acidity (mmol/g)
ChCl-p-TSA-DES-1	6.14
ChCl-p-TSA-DES-2	6.80
ChCl-p-TSA-DES-3	7.23
ChCl-p-TSA-DES-4	8.84
ChCl-Acetic acid DES-5	2.56
ChCl-Tartaric acid DES-6	2.32
ChCl-Oxalic acid DES-7	1.32

5.1.2 NMR spectroscopy of catalyst ChCl-p-TSA-DES-4 (molar ratio - 1:4)

The NMR results of prepared catalyst shows the presence of ChCl and p-TSA.

5.1.3 Catalyst screening for conversion of eugenol

Catalyst ChCl-p-TSA-DES-4 gave highest conversion of eugenol (90.42 %) owing to its high acidity. The catalyst ChCl-p-TSA-DES-4 was used in optimization studies.

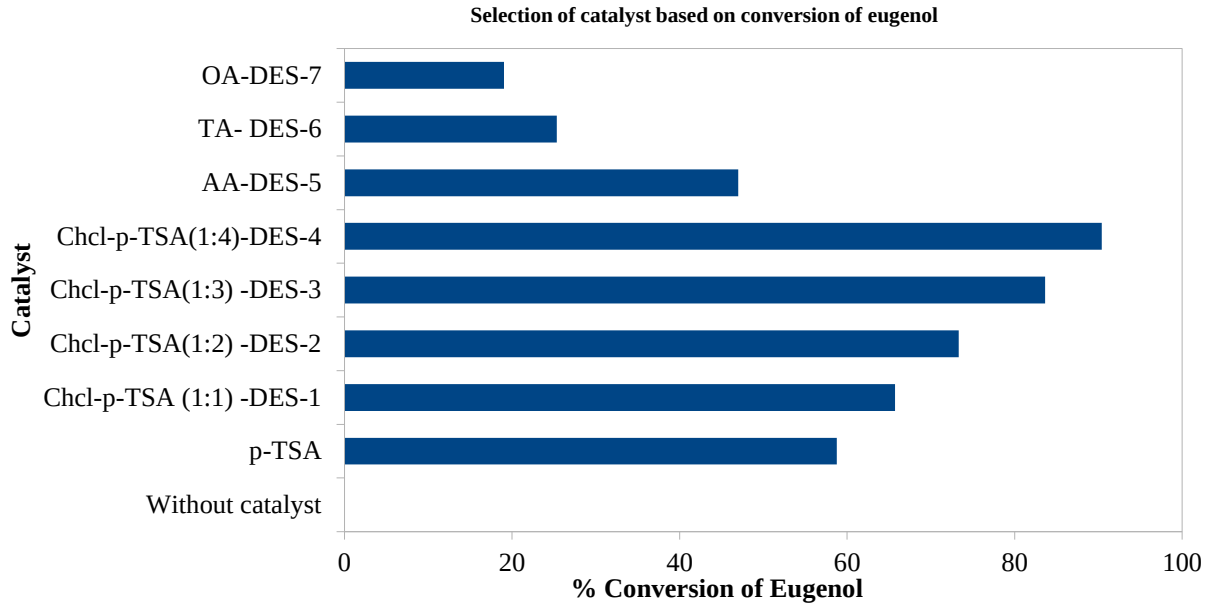

Fig.5.1.1. Selection of best catalyst for conversion of eugenol.

Reaction conditions: Eugenol: Benzoic acid = 1:5, Catalyst loading 0.02 g/cm^3, Speed of agitation-600 rpm, Temperature -110 ^{0}C, Reaction time- 3 h, Solvent-Toluene (30 ml).

5.1.4 Optimization of reaction parameters:

From catalytic screening studies, ChCl-p-TSA-DES-4, was found to be the most efficient catalyst. The effect of reaction parameters (mole ratio of eugenol to benzoic acid, catalyst loading, reaction time, and temperature) on the esterification of eugenol to maximize conversion was studied.

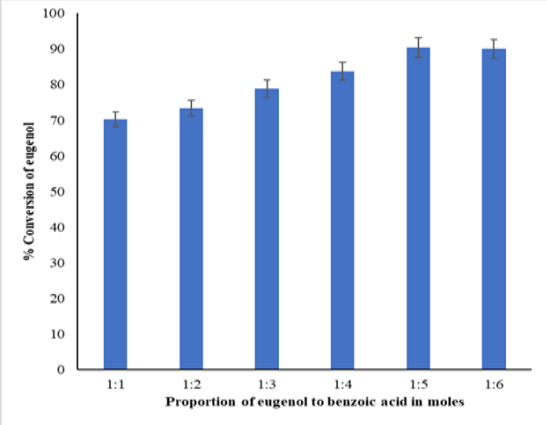

Fig 5.1.2: Effect of changing mole ratio of eugenol to benzoic acid on eugenol conversion

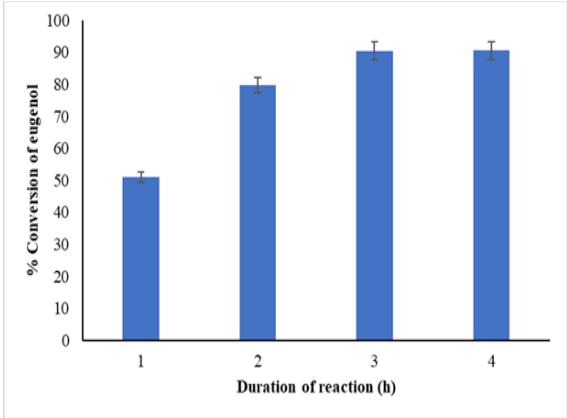

Fig 5.1.3. Effect of changing reaction time on eugenol conversion

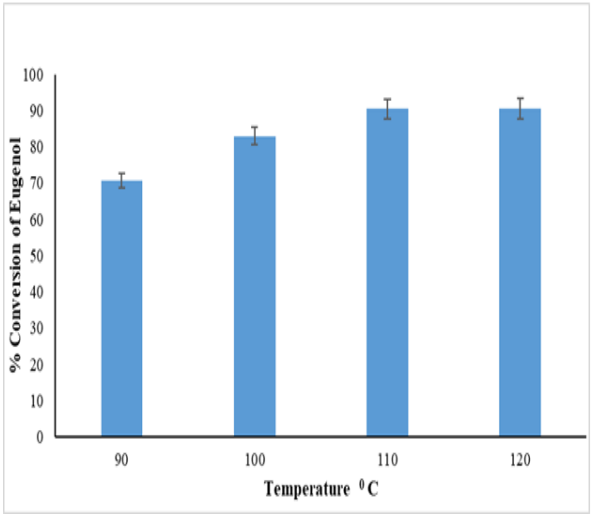

Fig 5.1.4: Effect of changing temperature on eugenol conversion

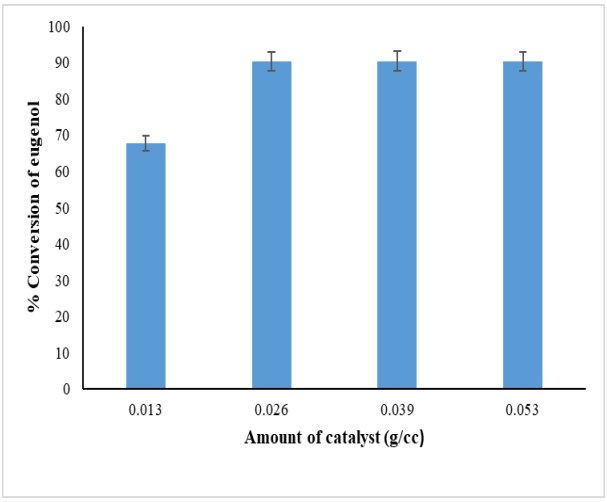

Fig 5.1.5: Effect of changing catalyst loading on eugenol conversion

Optimum values found to be:

Mole ratio of eugenol to benzoic acid - 1:5, Reaction time - 3 h, Temperature of reaction - 110°C Catalyst amount - 0.02 g/cm^3

The conversion of eugenol was found to be dependent mainly on reaction temperature and catalyst loading. When reaction temperature was increased from 100 °C to 110 °C. Conversion increased from 70.65 % to 90.42 %. The result suggests a kinetically controlled reaction. When the catalyst amount has risen from 0.01 to 0.02 g/cm^3, conversion increased from 67.78 % to 90.31 %.

5.1.5 Catalyst recycling studies:

The catalyst was separated from n-butanol by centrifugation and was air-dried. It was reused for five subsequent runs. Catalyst activity declined due to deposition of carbon on active sites. The experiments proved that catalysts could be easily separable and reusable.

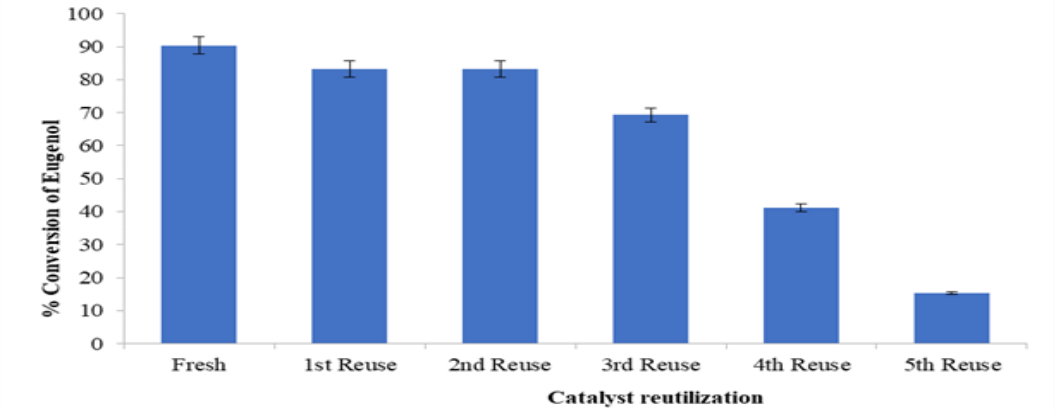

Fig 5.1.6: Catalyst recycling studies

Comparison with other catalysts

ChCl-p-TSA (1:4) DES gave 90.42 % conversion under optimized conditions. When compared with enzyme catalysts, DES required less time. As the DES catalyst is heterogeneous, it can be recovered easily compared with a homogeneous benzoyl chloride catalyst. The catalyst UDCaT-5 needs a complicated synthesis method and needs more time. DES could be easily synthesized and recovered from the reaction mixture. The catalyst ChCl-p-TSA(1:4) DES is superior to other reported catalysts.

Table 5.1.2: Comparison with other catalysts

Sr.No.	Catalyst	Reaction conditions					Conversion(%)	Yield(%)	Reference
		Mole ratio of eugenol to benzoic acid	Temp ^{0}C	Catalyst amount	Solvent volume(ml)	Time(hrs)			
1	Immobilized Staphylococcus aureus lipase	1:1.22	41	240 UI	4.6	6	100	70.83	Horchani *et al.*(2009)
2	Benzoyl chloride	--	--	--	--	--	100	87%	Sadeghian *et al*(2008)
3	UDCaT-5	1:5	110	0.012 g/cc	35 ml	4	90	--	Yadav *et al* (2012)
4	Our work	1:5	110	0.02 g/cc	30 ml	3	90.42	--	

5.1.6 Conclusion

The present work demonstrates a successful effort in utilizing acidic deep eutectic solvents as catalysts in biomass valorization. DESs based on choline chloride as HBA and carboxylic acids as HBD were synthesized and assessed for their catalytic activities in the conversion of eugenol to eugenol benzoate. Maximum conversion of Eugenol (90.42 %) was obtained with the catalyst ChCl-p-TSA-DES-4 under optimized reaction conditions (reaction time =3 h, mole ratio of eugenol to benzoic acid = 1:5, catalyst loading = 0.02g/cm^3, reaction temperature = 110 ^{0}C, Speed of agitation = 600 rpm). Reaction temperature and catalyst loading had prominent effect on conversion of eugenol, suggesting a kinetically controlled reaction. The catalyst, ChCl-p-TSA-DES-4, could be easily separated from reaction mixture and reused.

5.2 Scheme II: Alcoholysis of furfuryl alcohol to Butyl levulinate by using magnetic DES as catalyst

5.2.1 Acidity of catalyst

The proportion of HBA to HBD, the acid strength and variety of HBD, and intermolecular hydrogen bonds between HBD and HBA decided the acidity of prepared DES. $FeCl_3$ is acidic in nature; it also contributes to the acidity of DES. Catalyst MDES-3 (ChCl-4 p-TSAM-$FeCl_3$) displayed the highest acidity owing to highly acidic p-TSAM as HBD.

Table 5.2.1: Acidity of MDES

Name of DES	Acidity (mmol / g)
ChCl-Citric acid - $FeCl_3$ (MDES-1)	6.14
ChCl-Oxalic acid - $FeCl_3$ (MDES-2)	8.80
ChCl-4 p-TSAM-$FeCl_3$ (MDES-3)	9.51
ChCl-4 p-TSAM (DES)	8.84

5.2.2 Magnetic nature of catalyst:

The catalyst was mixed with 1,2-dichloromethane, and magnetic behavior was tested with an NdFeB magnet. As seen in Figure 1, the separation of the catalyst from the liquid mixture was easier.

Figure 5.2.1: Magnetic behaviour of catalyst

5.2.3 Nuclear Magnetic Resonance Spectroscopy

^{1}H and ^{13}C NMR spectra clearly identifies choline chloride and p-TSAM in MDES. As evident from NMR studies, the structure of individual constituents of MDES-3 did not change. Presence of hydrogen bonding between ChCl and p-TSAM and presence of highly electronegative chlorine

atoms (in ChCl and $FeCl_3$) may have caused deshielding . This may have moved peaks in both ^1H and ^{13}C NMR to higher frequencies.

5.2.4 Fourier-transform infrared spectroscopy (FT-IR)

Compared to reported spectra of choline chloride, peaks were obtained at lower wavelengths in spectra of MDES-3. Due to formation of hydrogen bonds between components, peaks broadened and shifted, confirming formation of a stable DES.

Transmittance (%T) versus wavenumber (cm^{-1})

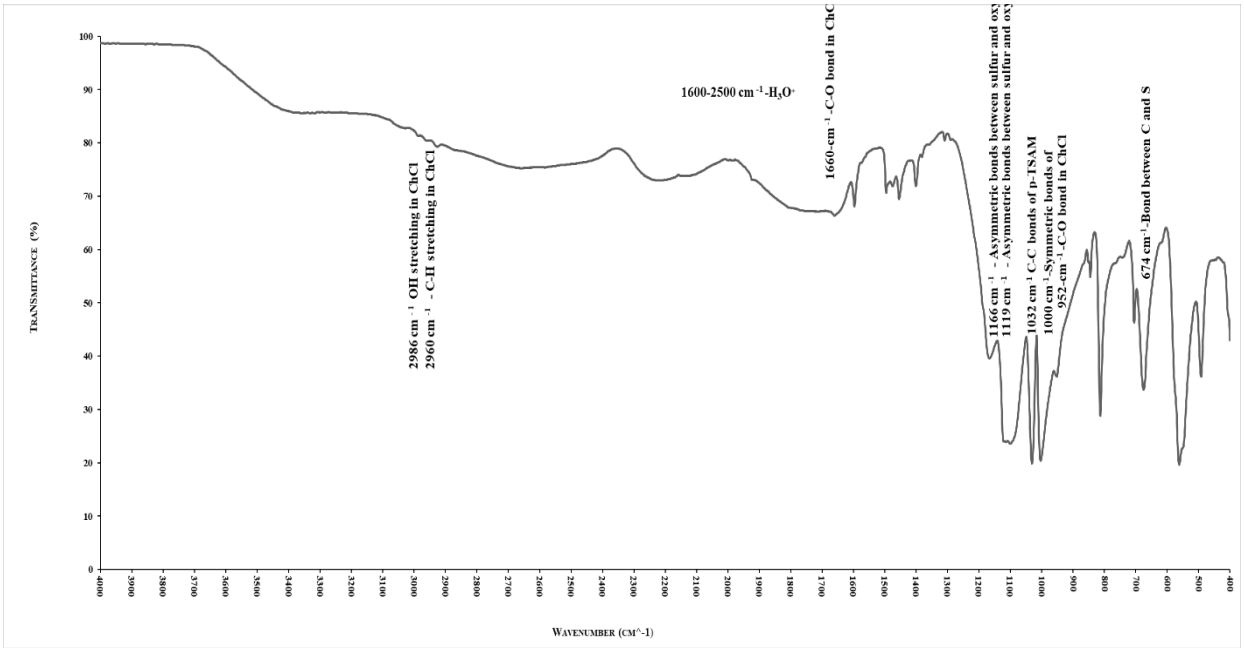
TRANSMITTANCE (%)
WAVENUMBER (CM^-1)
1600-2500 cm -1-H3O+
1660-cm -1 -C-O bond in ChC
2986 cm -1 OH stretching in ChCl
2960 cm -1 - C-H stretching in ChCl
1166 cm -1 - Asymmetric bonds between sulfur and oxy
1119 cm -1 - Asymmetric bonds between sulfur and oxy
1032 cm -1 C-C bonds of p-TSAM
1000 cm -1-Symmetric bonds of
952-cm -1-C-O bond in ChCl
674 cm -1-Bond between C and S

Figure 5.2.2: FTIR spectra for the catalyst MDES-3 (ChCl-4 p-TSAM-$FeCl_3$).

5.2.5 Selection of best catalyst for synthesis of n butyl levulinate from furfuryl alcohol

When catalyst was not used, the reaction between furfuryl alcohol and n-butanol did not occur. Figure 5 shows BL yield by alcoholysis of FAL using different catalysts. The highest yield of 98.43 % was obtained with catalyst MDES-3 (ChCl-4 p-TSAM-$FeCl_3$) as it possesses the highest acidity. The catalyst MDES-3 (ChCl-4 p-TSAM-$FeCl_3$) was used in optimization studies.

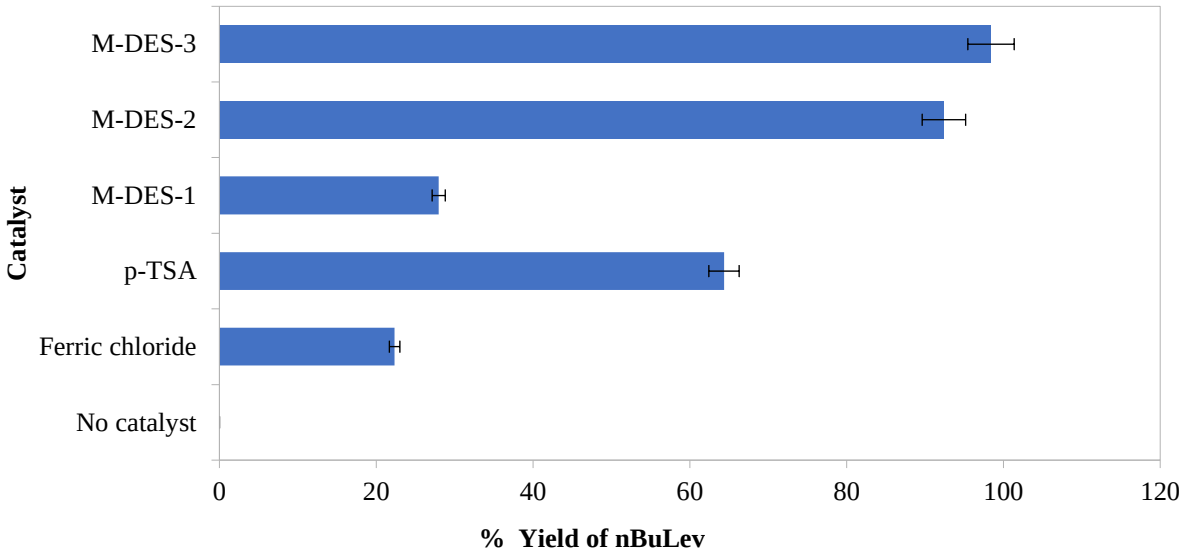

Figure 5.2.3: Selection of best catalyst for conversion of FAL into n-BL.

Reaction parameters: FAL: n-BuOH ratio (molar units) = 1:20, catalyst quantity = 0.02 g/cm^3, temperature = 120 ^{0}C, time for reaction = 3 h.

5.2.6 Result of changing reaction parameters on the conversion of furfuryl alcohol

From catalytic screening studies, MDES-3 (ChCl-4 p-TSAM-$FeCl_3$) was able to catalyze reaction efficiently. To maximize n-BL(nBuLev) yield, optimization studies were carried out to maximize by varying reaction parameters (FAL: n-BuOH ratio (molar units), catalyst quantity, time of reaction, and temperature).

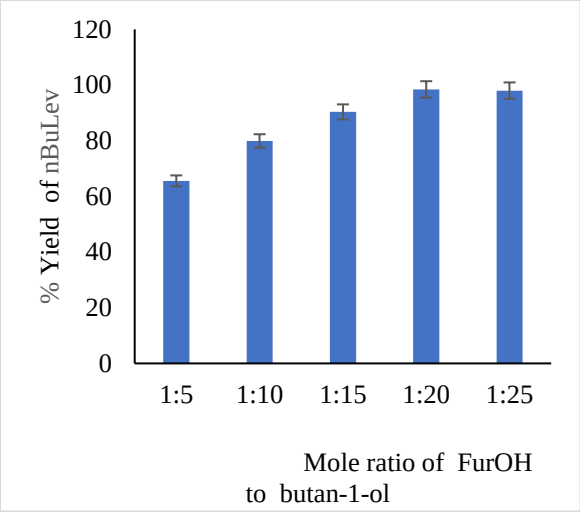

Figure 5.2.4: Result of varying mole ratio of furfuryl alcohol: n-butanol on n-BL yield

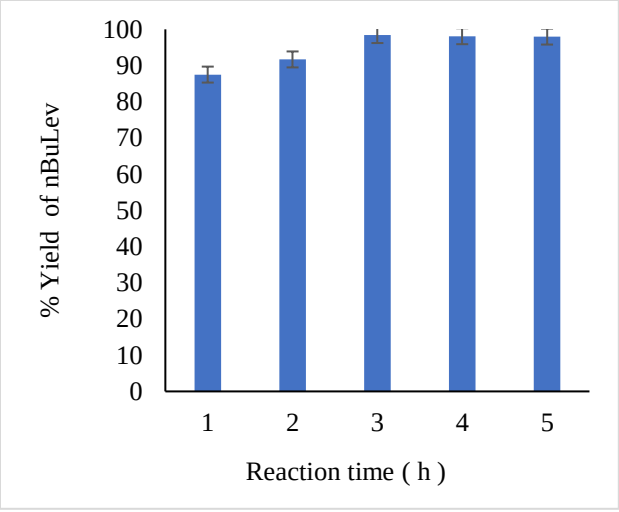

Figure 5.2.5: Result of varying time of reaction on n-BL yield

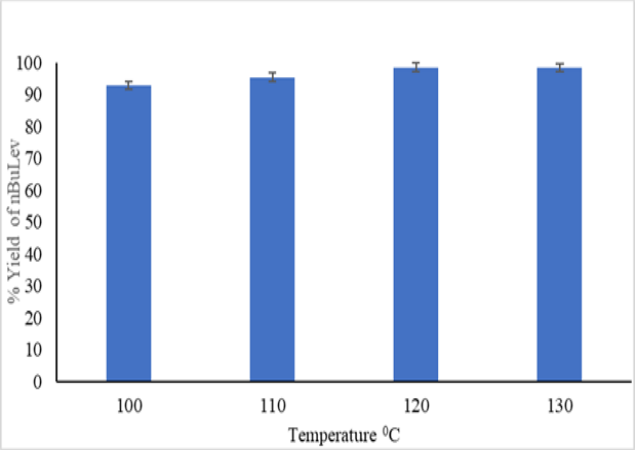

Figure 5.2.6: Result of varying temperature of reaction on n-BL yield

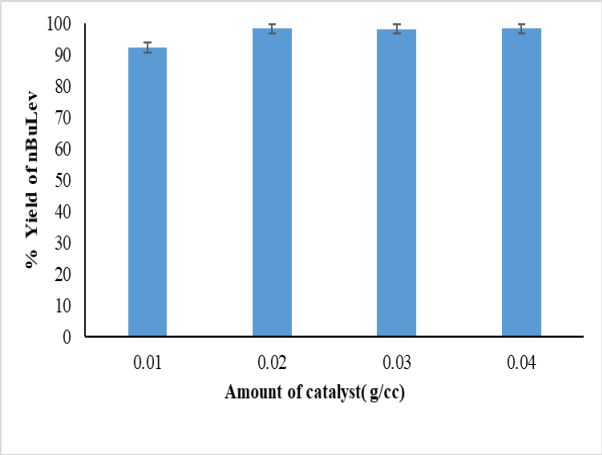

Figure 5.2.7: Result of varying catalyst quantity on n-BL yield

Optimum values found to be:

Mole ratio of FAL:n-BuOH - 1:20

Reaction time - 3 h

Temperature of reaction - 120°C

Catalyst amount - 0.02 g/cm^3

The temperature of reaction, FAL: n-BuOH ratio (molar units), and amount of catalyst strongly affected BL yield. Conversion rose from 92.83 %. to 98.41 % with increase in temperature from 100 °C to 120° C. The result suggests a kinetically controlled reaction. When the concentration of catalyst was raised from 0.01 to 0.02 g/cm^3, conversion improved from 92.35 % to 98.42 % . The mole ratio of FAL:n-BuOH influenced selectivity to the formation of BL In the first hour of the reaction, the selectivity to BL was low, and a large amount of intermediate BMF was formed. As the reaction proceeded, selectivity to BL increased.

5.2.11 Catalyst recycling studies:

As MDES-3 catalyst was magnetic, its separation from reaction mixture was facilitated by a magnet. Washing of the catalyst was done with n-butanol to remove humins. It was then air dried and reused. Catalyst activity declined by 6.25% in second run and 9.16 % in third run. The study proved that catalyst can be reused three times. Low BL yield in third run might be due to carbon deposition on active sites of catalyst.

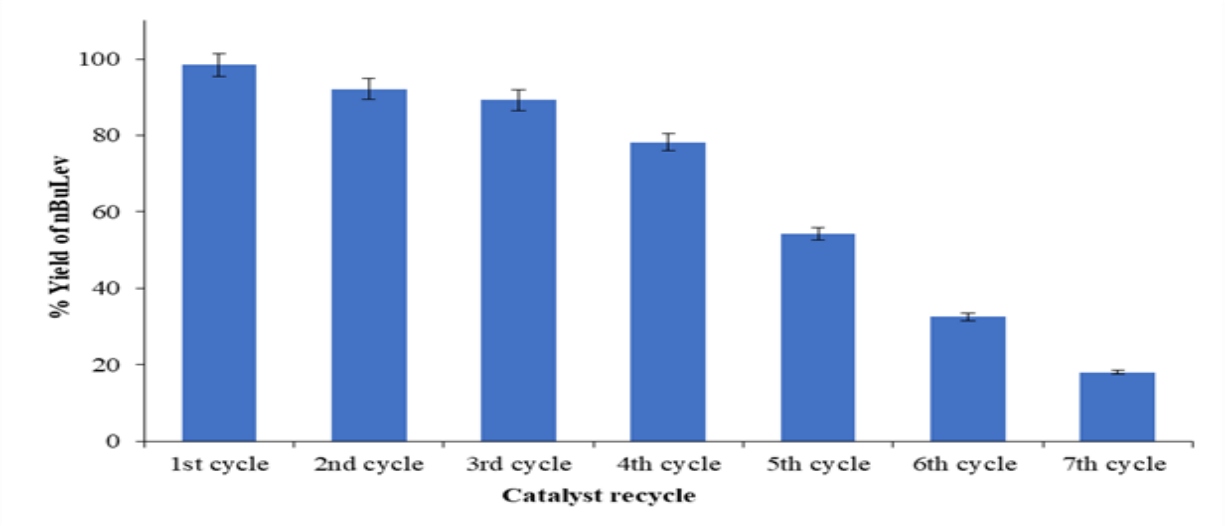

Fig.5.2.8: Catalyst recycling studies

Comparison with other catalysts

ChCl-p-TSAM-$FeCl_3$(1:4:0.5) DES gave 98.42 % yield under optimized conditions. While graphite oxide catalyst was needed in lowest amount, it lost its activity due loss of acidic groups and needed more amount of n-butanol. Catalyst PTA/HAC needed low amount of n-BuOH but gave low conversion. Compared to other catalysts, our catalyst needed 3 hrs for completion of reaction. The catalyst ChCl-p-TSAM-$FeCl_3$(1:4:0.5) DES gave better performance compared to other reported catalysts.

5.2.12 Conclusion

Green synthesis of FAL to BL by using easily recyclable magnetic deep eutectic solvents was studied. Among various catalysts prepared, MDES-3 composed of p-toluenesulfonic acid monohydrate, ferric chloride and choline chloride proved to be most efficient catalyst. Under optimized conditions (mole ratio of FAL to n-BuOH = 1:20, catalyst quantity = 0.02 g/cm^3 , temperature = 120 ^{0}C, time of reaction = 3 hrs.), maximum BL yield was 98.42%.Magnetic nature of catalyst helped its separation from reaction mixture. The catalyst was used thrice with 15.41 % drop in BL yield in third cycle.

5.3 Scheme III-

Esterification of Levulinic acid (LA) to Butyl levulinate by using CTAB based DES

Catalyst: CTAB-carboxylic acid based hydrophobic DES with CTAB as HBA and carboxylic acids (citric, oxalic, p-TSAM) as HBD.

5.3.1 Acidity of HDES

Acidity of the catalyst CTAB -p-TSAM (HDES-1) was high due to higher proportion of strong acid i.e., p-TSAM. Lowest acidity was obtained for CTAB-Citric acid (HDES-3) [25–27][26–28].

Table 5.3.1: Acidity of HDES

Name of HDES	Acidity (mmol/g)
CTAB-p-TSAM (1:3)- HDES-1	6.72
CTAB- Oxalic acid (1:6)-HDES-2	4.13
CTAB- Citric acid (1:6)-HDES-3	2.17

5.3.2 NMR spectroscopy of catalyst HDES-1(CTAB:p-TSAM =1:3)

The NMR analysis shows that structure of individual components did not change during formation of HDES-1.

5.3.3 FTIR spectroscopy of HDES-1(CTAB:p-TSAM =1:3)

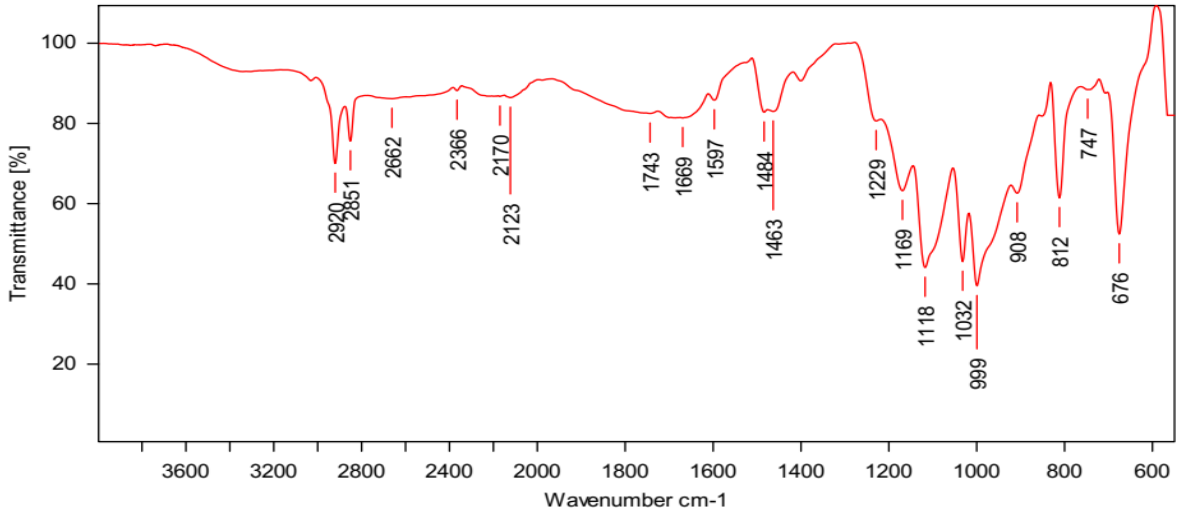

Figure 5.3.1: Fourier Transform Infra-Red spectra for the fresh catalyst HDES-1(CTAB:p-TSAM =1:3).

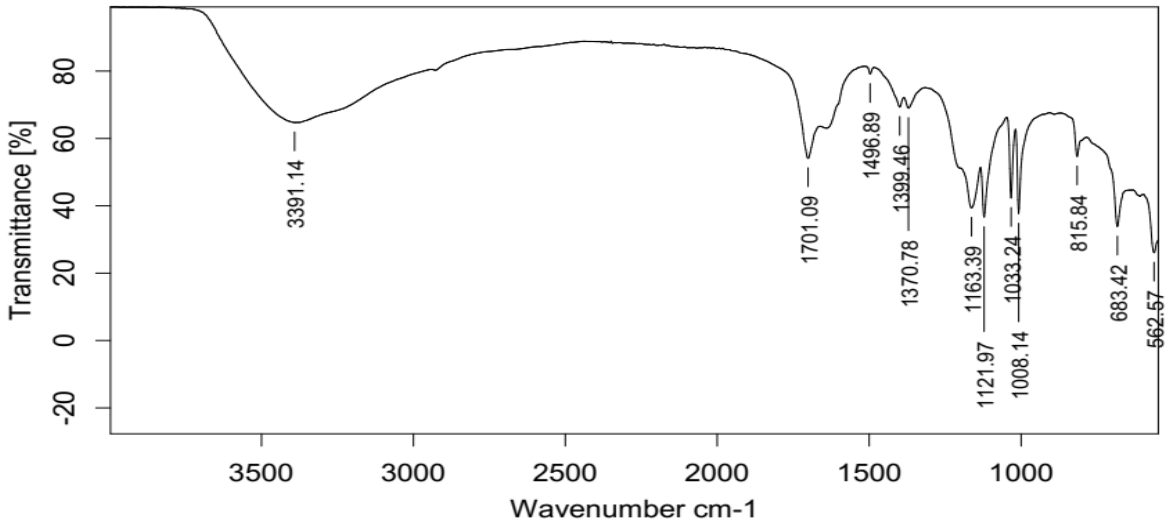

Figure 5.3.2: Fourier Transform Infra-Red spectra for the reused catalyst HDES-1(CTAB:p-TSAM =1:3).

The FTIR spectra proved successful formation of DES between CTAB and p-TSAM.

5.3.4 Assessment of catalytic activity of HDES in synthesis of n-BL

The results of catalytic reaction between LA and n-BuOH are shown in Figure 4. When CTAB alone was used as a catalyst, no conversion was obtained. With p-TSAM as catalyst, LA conversion was 71.39 %. The highest conversion of 88.77 % was obtained with catalyst HDES-1(CTAB-p-TSAM (1:3)).

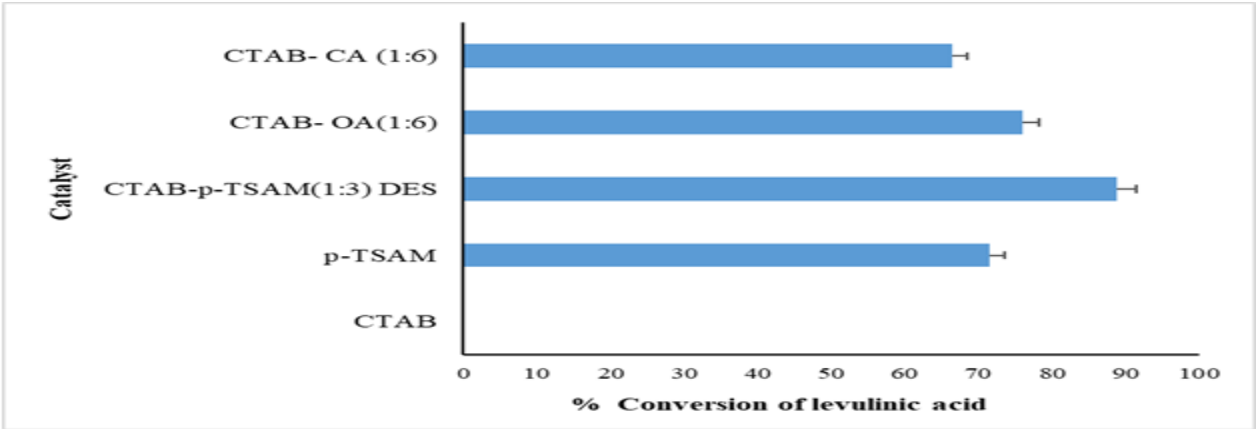

Figure 5.3.3: Assessment of catalytic activity in the reaction between levulinic acid (LA) and n-butanol(n-BuOH) to synthesize butyl levulinate (BL). Ratio of LA to n-BuOH (in moles) = 1:5, amount of catalyst = 0.01 g/cm^3, speed of stirring = 600 rpm, temperature = 120 ^{0}C, time = 3 h.

5.3.5 Optimization of reaction parameters to maximize levulinic acid (LA) conversion

Results from catalytic activity studies proved that HDES-1(CTAB-p-TSAM (1:3)) was able to give the highest LA conversion. This catalyst was subjected to optimization studies to maximize LA conversion by varying the ratio of moles of LA: nBuOH, amount of catalyst, time duration for reaction, and temperature of the reaction.

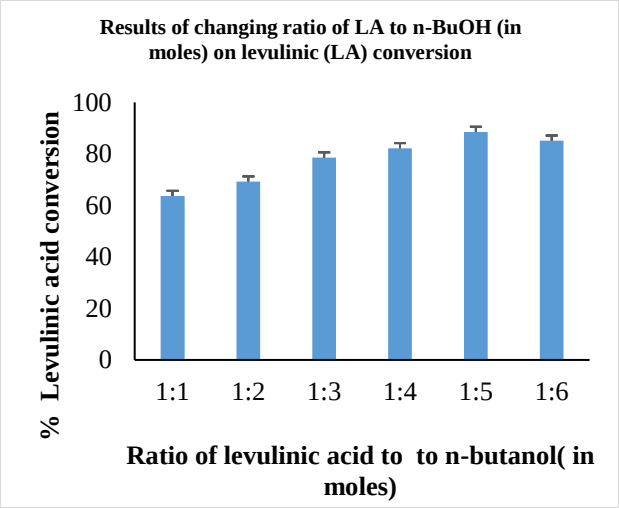

Figure 5.3.4: Effect of changing mole ratio of LA to n-BuOH on levulinic acid (LA) conversion

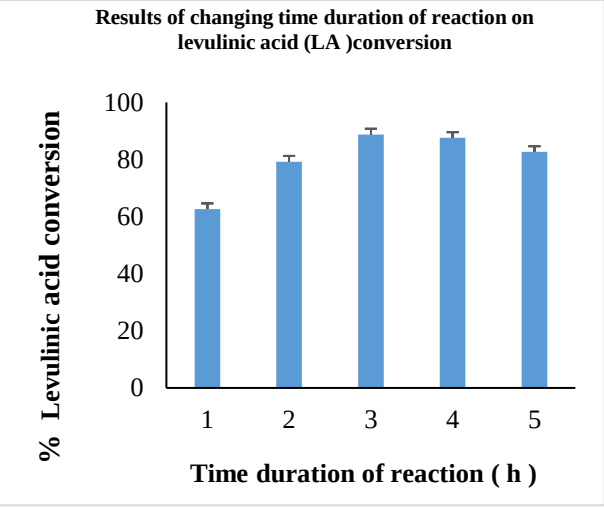

Figure 5.3.5: Results of changing time duration of reaction on levulinic acid (LA) conversion

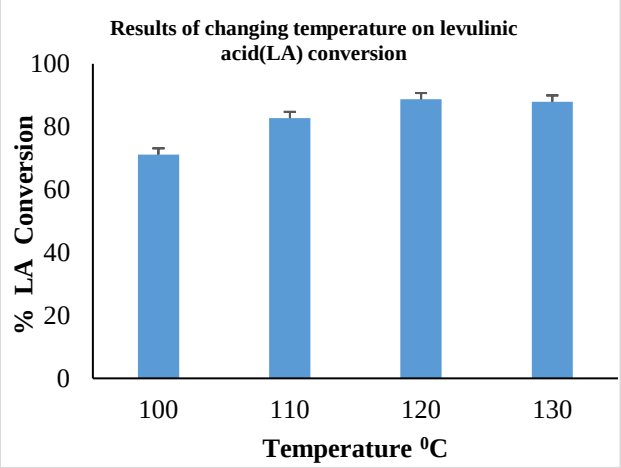

Figure 5.3.6: Results of changing temperature of reaction on levulinic acid (LA) conversion

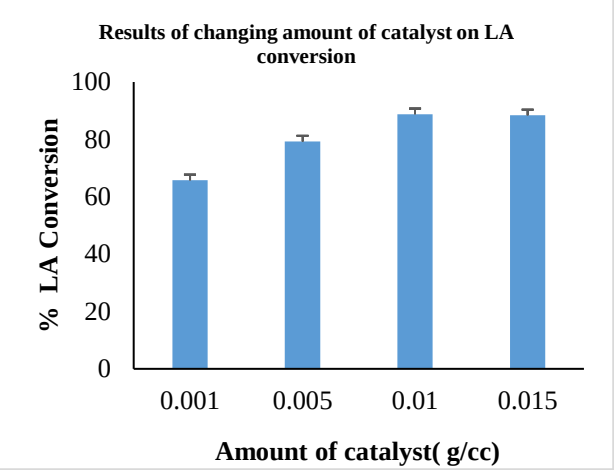

Figure 5.3.7: Results of changing amount of catalyst on levulinic acid (LA) conversion

Optimum values found to be:

The mole ratio of LA:n-BuOH - 1:5

Reaction time - 3 h

Temperature of reaction - 120°C

Catalyst amount - 0.01 g/cm^3

Optimization studies showed that LA conversion was greatly affected by the ratio of LA to n-BuOH (in moles), reaction temperature, and catalyst amount.

5.3.6. Catalyst reusability studies:

The study demonstrates that catalyst activity slightly decreased after being reused 5 times. However, after 6th run, catalyst activity declined to an appreciable extent. FTIR for recovered catalyst after the 7th run was carried out. FT-IR images of recycled catalysts (after the 7th cycle) are represented in 5.3.1(B).FT-IR for recycled catalyst showed decreased intensities and shifting of peaks. Peaks for asymmetric and symmetric stretching of SO_3 and C-S bending in p-TSAM were observed. C-H and N-H stretching peaks in CTAB were absent in the spectra of recycled CTAB-p-TSAM DES. It is clear from the comparison that the catalyst structure did not change appreciably till the 5th recycling. There might be a loss of a few SO3 groups in HDES after the 7th run. Peaks for N-H and C-H stretching for CTAB were not observed in FT-IR spectra of recycled catalyst. CTAB carbon chains may have been modified due to the solvation effects of water.

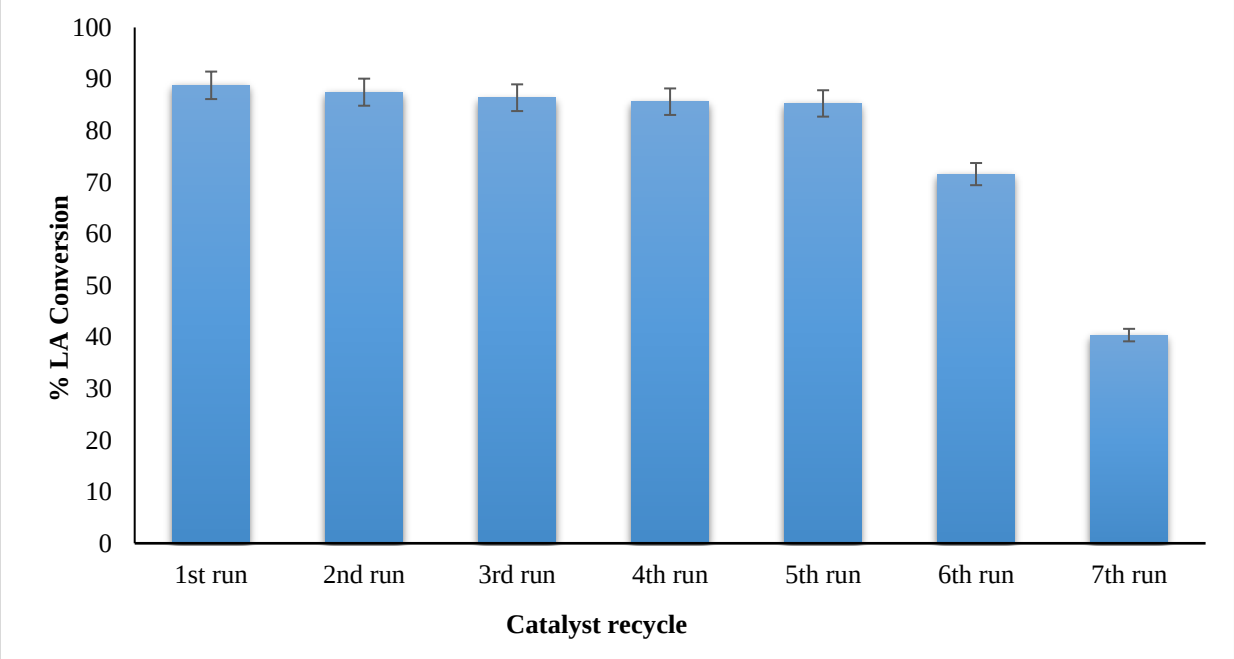

Figure 5.3.8: LA Conversion as a function of catalyst recycle. Conditions for the reaction: Ratio of LA to n-BuOH (in moles) = 1:5, amount of catalyst = 0.01 g/cm^3, speed of stirring = 400 rpm, temperature = 120 ^{0}C, time duration of reaction = 3 h.

Comparison with other catalysts

High LA conversion was obtained with aluminium sulfate, sulfonic acid-functionalized lignin-montmorillonite complex, Halloysite, Magnetic nano-solid acid catalyst, TPA -Zirconium oxide-silica as catalysts. These reported catalysts are either homogeneous or complex and require time-consuming synthesis methods. In contrast, the CTAB-pTSAM DES catalyst was easy to synthesize and separate from the reaction mixture and gave good LA conversion within three hours under conventional heating.

Conclusion:

In the research work presented here, HDES were synthesized using CTAB as HBA and various acids as HBD. They were employed as catalysts in the esterification reaction between levulinic acid and n-butanol to prepare butyl levulinate. Synthesis, regeneration, and reuse of catalysts were carried out by adhering to principles of green chemistry. The catalyst HDES-1 was found to be the most efficient. It gave a maximum LA conversion of 88.77%. The results prove that CTAB-p-TSAM based HDES provided enough Bronsted acid sites to carry out esterification reaction. Optimization of reaction parameters was carried out to obtain maximum LA conversion. The ratio of LA to n-BuOH (in moles), reaction temperature, and amount of catalyst influenced LA conversion to a greater extent. Ease of recovery and reuse might prove to be an attractive trait for developing further applications of CTAB-p-TSAM HDES.

5.4 Scheme IV: Aldol Condensation of the furfural with acetone by using basic DES as a catalyst

Results:

5.4.1: Alkalinity of BDES

Catalyst K_2CO_3:EG(1:6) showed maximum alkalinity. This catalyst was selected for NMR and FTIR analysis.

Table 5.4.1- Alkalinity of BDES

DES		Alkalinity mmol/g
BDES-1	K_2CO_3:EG(1:6)	5.70
BDES-2	K_2CO_3:EG(1:8)	4.5
BDES-3	K_2CO_3:EG(1:10)	3.43

BDES could not form at K_2CO_3:EG mole ratio of 1:1,1:2,1:3,1:4,1:5.

EG-Ethylene glycol;

K_2CO_3-Potassium carbonate

5.4.2 NMR studies on catalyst B-DES-1

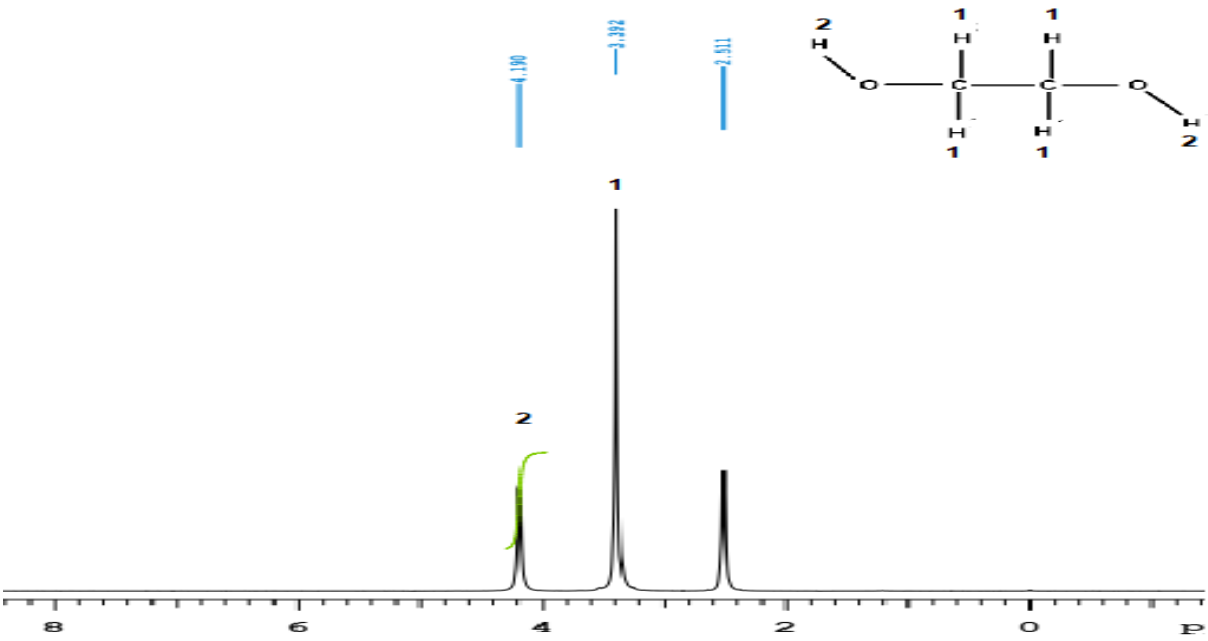

Figure 5.4.1: NMR (^{1}H) spectra for the catalyst BDES-1**.**

^{1}H NMR spectra of B-DES-1(Figure 4.4.1) shows 4 protons in methylene groups of EG at 3.392 ppm. Protons in hydroxyl groups are represented by peak at 4.19 ppm. DMSO is identified by signal at 2.511 ppm

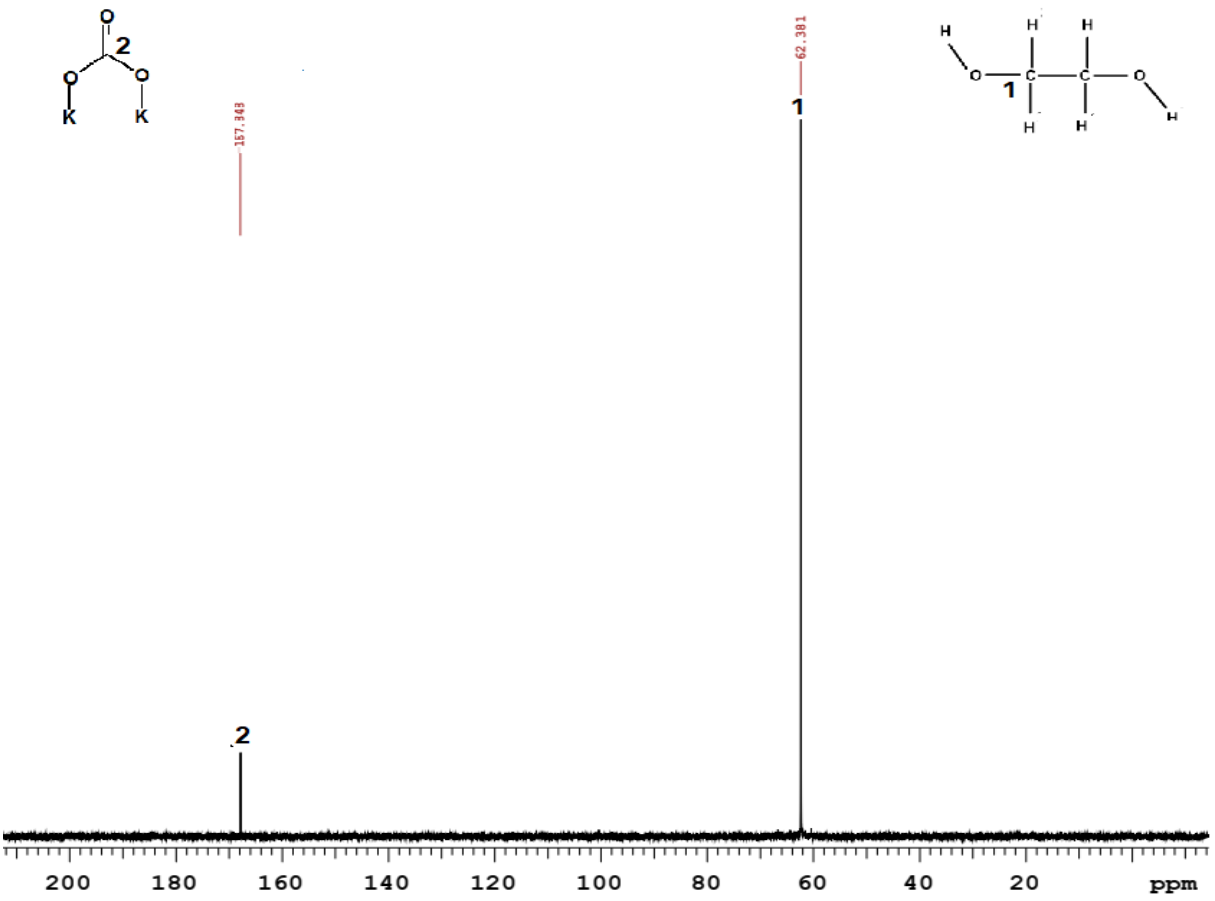

Figure 5.4.2: ^{13}C NMR spectra for the B-DES-1 catalyst.

The ^{13}C spectrogram of B-DES-1, shown in Figure 5.4.2, reveal signals for carbons in EG at 62.38 ppm. Carbonate group in potassium carbonate is represented by signal at 167.85 ppm. Yi Zhou *et al.*(2024) reported two new signals for methylene carbons and one peak for carbonyl carbon in EG based carbonate in ^{13}C NMR spectra. Such signals were absent in spectra obtained in this research. Both spectrograms prove molecular arrangement of components remained unchanged in B-DES. To study whether formation of EG based carbonate occurs, FTIR analysis was carried out.

5.4.3 FTIR of catalyst BDES-1(K_2CO_3:EG(1:6))

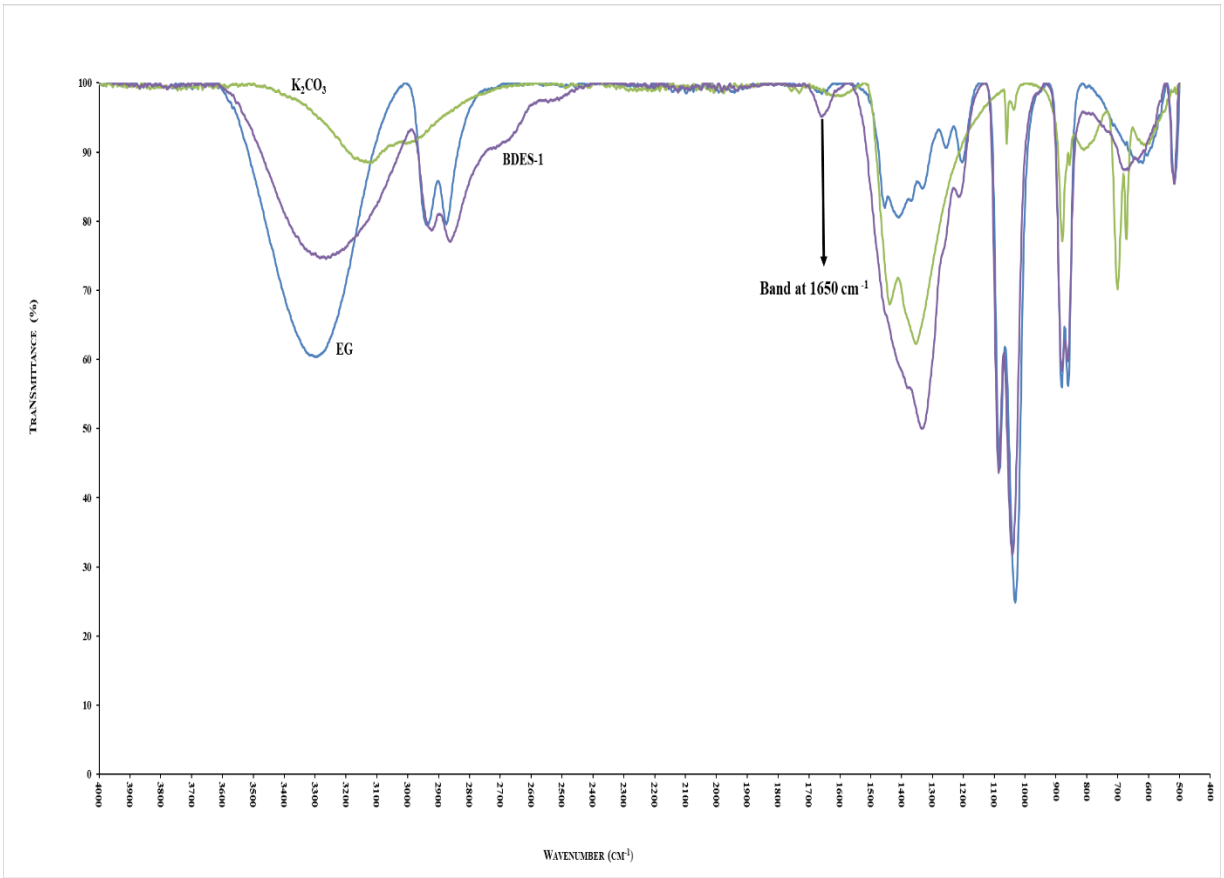

Figure 5.4.3: FTIR spectra of catalyst K_2CO_3:EG(1:6)

The formation of basic DES is confirmed by the appearance of a new band at 1650 cm-1, which shows the C=O asymmetrical stretching mode of ROCOO ¯.This suggests the formation of EG-based carbonate.

5.4.4 Catalyst screening for conversion of furfural

From catalyst screening, catalyst K_2CO_3 has the highest furfural conversion. As this catalyst was homogeneous, it was not used for further studies. The catalyst BDES-1(K_2CO_3:EG(1:6)) gave 89.47% furfural conversion. Catalyst K_2CO_3:EG(1:6) (BDES-1) was selected for optimization

studies.

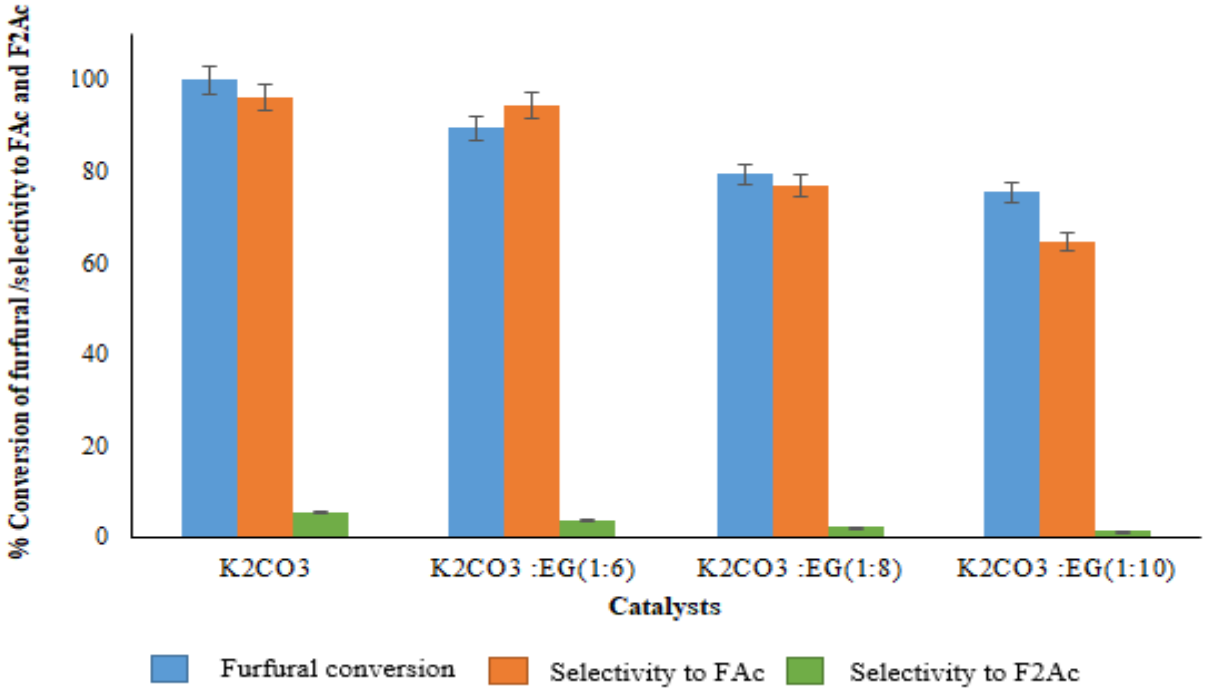

Figure 5.4.4: Identifying the most effective catalyst for obtaining highest conversion of furfural**.** **Experimental variables**: Molar proportion of furfural to acetone = 0.1 :1, amount of catalyst = 4 x 10^{-2} g/cc, temperature = 60 ^{0}C, speed of stirring = 400 revolutions per minute, duration of reaction = five hours.

It also showed high selectivity for FAc. Its highly basic nature helped in achieving high conversion.

5.4.5 Optimization of reaction parameters to maximize conversion of furfural

Results from catalytic activity studies proved that BDES-1(K_2CO_3 :E(1:6)) was able to give the second-highest furfural conversion. This catalyst was subjected to optimization studies to maximize furfural conversion by varying the ratio of moles of furfural: acetone, amount of catalyst, time duration for reaction, and reaction temperature.

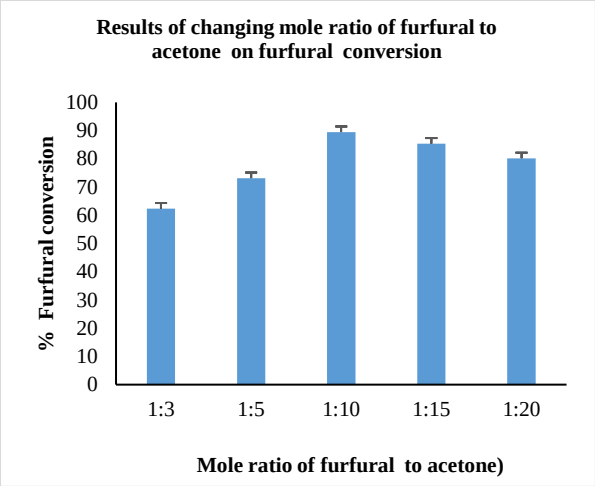

Figure 5.4.5: Result of varying mole ratio of furfural to acetone on furfural conversion

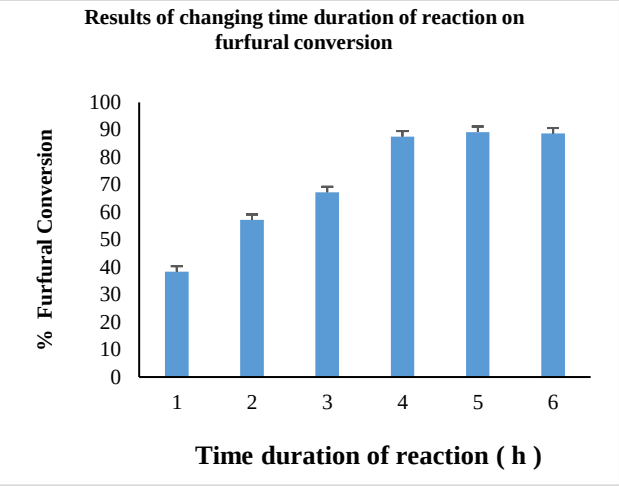

Figure 5.4.6: Result of different times of reaction on furfural conversion

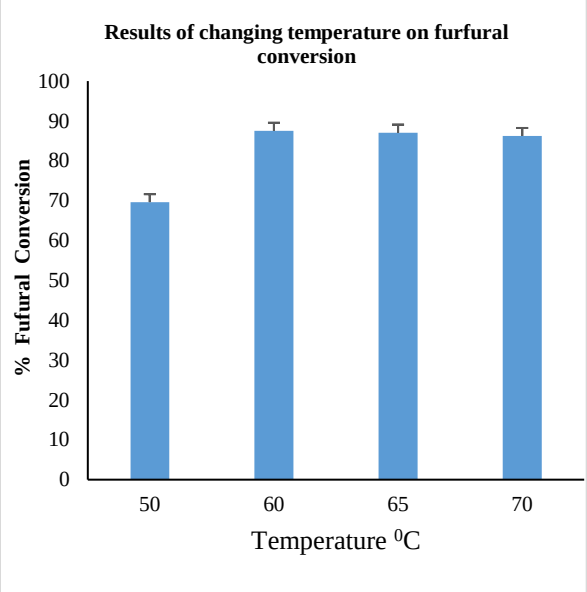

Figure 5.4.7: Result of varying temperature on furfural conversion

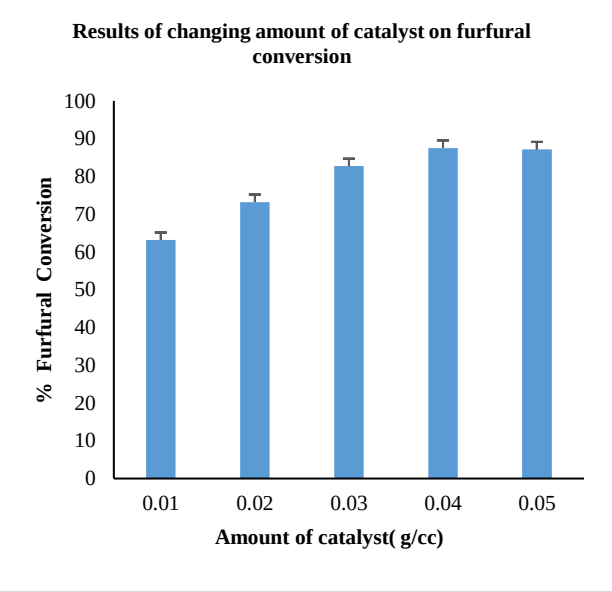

Figure 5.4.8: Result of varying catalyst amount on furfural conversion

Optimum values found to be:

Mole ratio of furfural to acetone - 1:5

Reaction time - 4 h

Temperature of reaction - 60°C

Catalyst amount = 0.04 g/ cm^3

From optimization studies, it was seen that furfural conversion was greatly affected by reaction time, reaction temperature, and catalyst amount.

Catalyst recycling studies:

The catalyst's performance remained stable through the third cycle. However, by the sixth cycle, the furfural conversion dropped to just 40%. This reduction in conversion could be ascribed to the accumulation of carbonaceous residues on the catalyst's active sites. Catalyst activity declined from 89.78% to 58.15%.

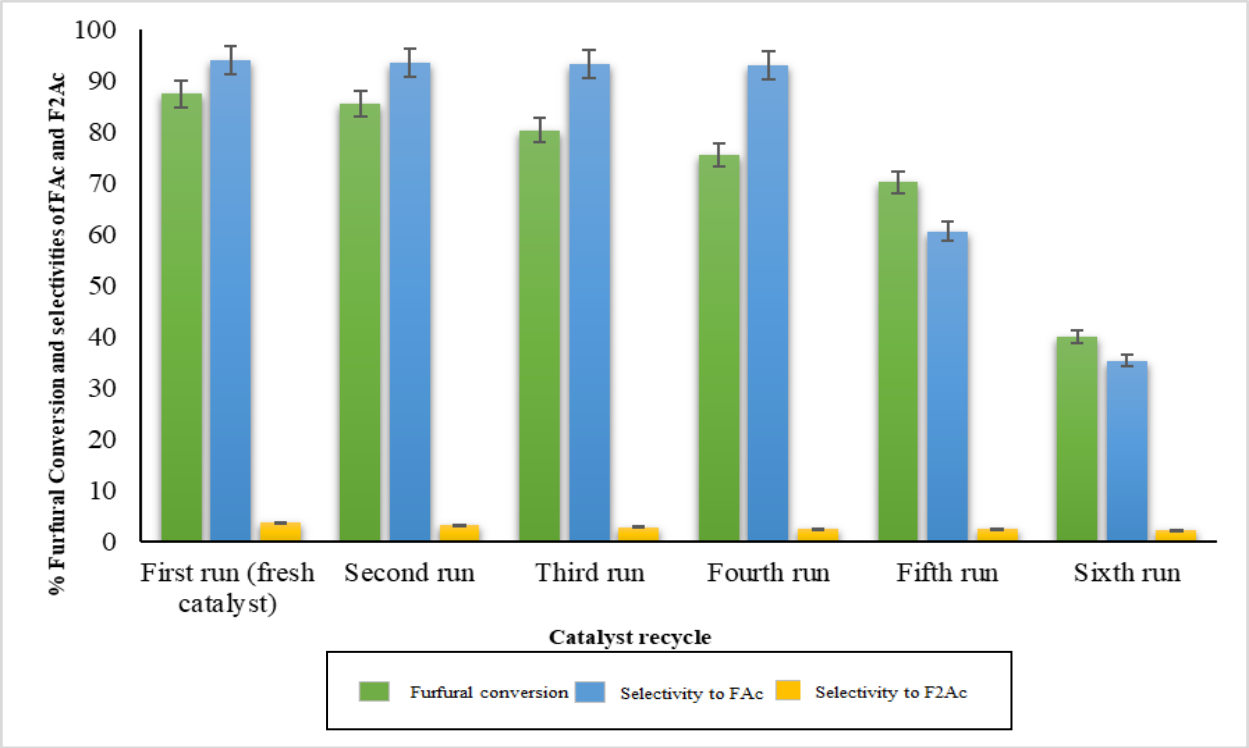

Figure 5.4.9: Catalyst recycling studies

The FT-IR spectra comparing fresh B-DES-6 and the recycled catalyst after the sixth cycle are presented in Figure 5.4.10. Analysis revealed that the catalyst preserved its structural integrity, though the transmittance intensity decreased, and peak positions shifted.

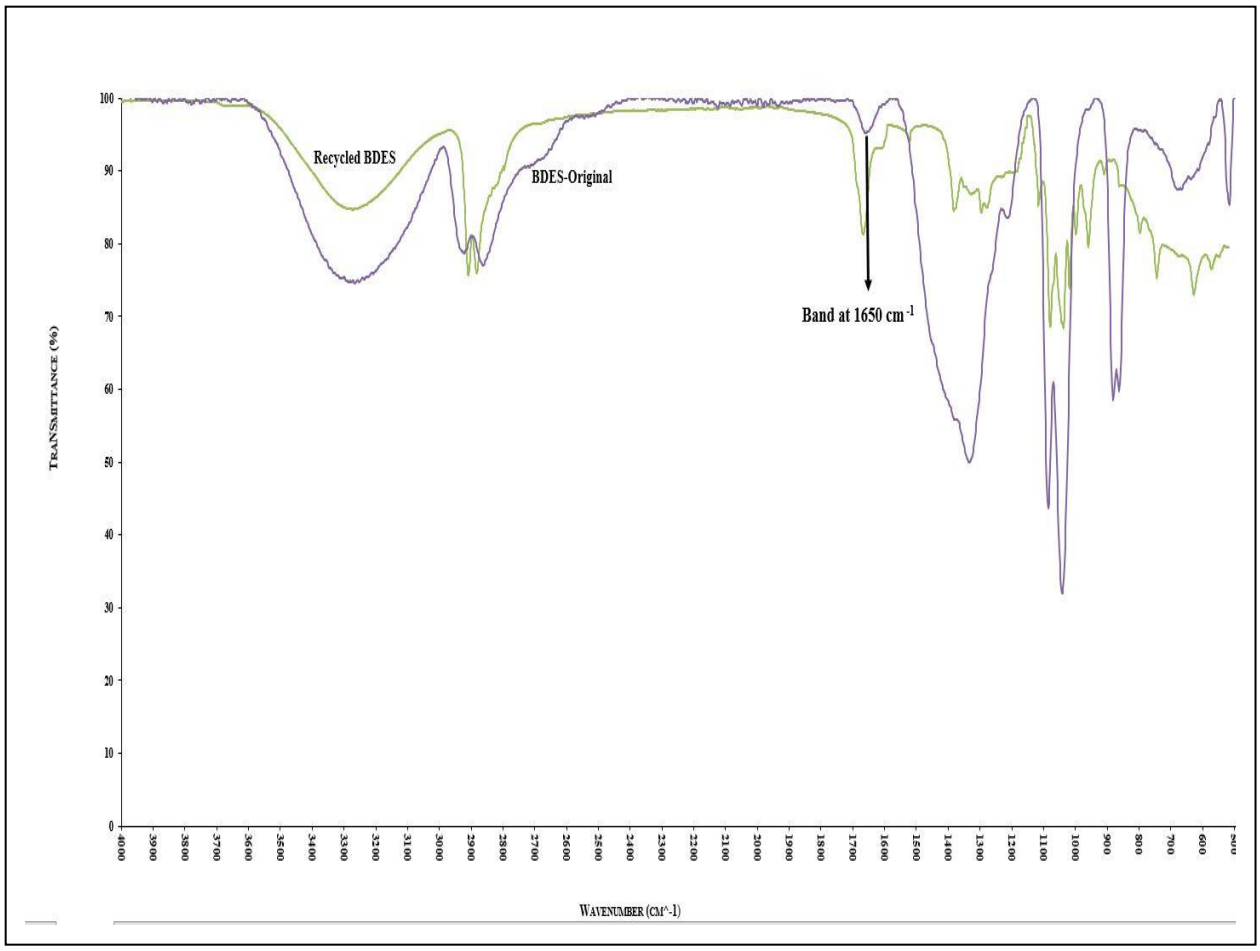

Figure 5.4.10: Infrared spectroscopy of recycled B-DES-6 using Fourier transform (FTIR).

Comparison with other catalysts

Catalysts reported in the literature required more reaction time and complex synthesis methods and gave lower conversion and yield. Compared to other catalysts, BDES required less time, gave more conversion, and was easy to synthesize.

Conclusion:

This research demonstrates the first instance of using basic DES composed of $K2CO_3$ and ethylene glycol in the synthesis of furfural acetone through aldol condensation of furfural. The catalyst K_2CO_3:EG(1:6) gave 87.56% conversion under optimized conditions. Compared with other catalysts, this catalyst was easier to synthesize and separate from the reaction mixture and gave high conversion.

6. CONCLUSION

The major focus of researchers is to improve catalyst performance in biomass valorization. With well-designed catalysts, biomass refineries will become economical and profitable. Catalysts used in biomass transformations are usually expensive, give lower conversion and yields, and are challenging to synthesize and separate from the reaction mixture. Some of these catalysts are toxic. Current research focused on the synthesis of novel deep eutectic solvents and testing them as catalysts in biomass valorization. Four reaction schemes were identified:

1) Synthesis of eugenol benzoate from eugenol and benzoic acid using choline chloride-based acidic DES as catalysts-Choline chloride-p-TSA(mole ratio 1:4) was the best catalyst.
2) Alcoholysis of furfuryl alcohol to butyl levulinate using magnetic DES as catalysts-Magnetic DES composed of ChCl-p-TSAM-$FeCl_3$ (1:4:0.5) was the best catalyst.
3) Esterification of levulinic acid to butyl levulinate using CTAB-based hydrophobic DES as catalysts-CTAB-p-TSAM(mole ratio – 1:3) was the best catalyst.
4) Aldol condensation of furfural and acetone using potassium carbonate and ethylene glycol-based basic DES as catalysts-Catalyst K_2CO_3-EG(mole ratio – 1:6) was the best catalyst

The best catalyst was identified, characterized, and subjected to optimization and recycling studies in each scheme. The research will open new avenues for applications of DES in biomass conversion reactions. It will reduce the costs of chemical conversions and produce bio-derived chemicals cheaply.

7. Future Scope

The current work has demonstrated the efficient catalytic nature of DES in biomass conversion, focusing on specific reactions. However, further exploration of diverse reactions and DES types is warranted, given their properties and versatility. While these studies were conducted on a laboratory scale, the promising performance of DES highlights their potential for industrial process development, emphasizing the need for scaling up and optimizing their application in commercial scale.

8: Publications

The work has resulted in 3 Paper published, 2 under preparation

1) Esterification of lignin-derived phenolic compound eugenol to eugenol benzoate using acidic deep eutectic solvent as a catalyst

- R. Joshi and M. S. Tiwari, "Esterification of lignin-derived phenolic compound eugenol to eugenol benzoate using acidic deep eutectic solvent as a catalyst," Chemical Papers, vol. 78, no. 18, pp. 9497–9505, Dec. 2024. doi: 10.1007/s11696-024-03762-2.

2) Biobased synthesis of butyl levulinate from levulinic acid by using CTAB-based hydrophobic deep eutectic solvent as a catalyst

- R. Joshi and M. S. Tiwari, "Biobased synthesis of butyl levulinate from levulinic acid by using CTAB-based hydrophobic deep eutectic solvent as a catalyst," Biomass Conversion and Biorefinery, 2024, published 18 Dec. 2024. doi: 10.1007/s13399-024-06429-w.

3) Upgradation of hemicellulose-derived furfuryl alcohol to butyl levulinate by using magnetic acidic deep eutectic solvents as catalysts

- R. Joshi and M. S. Tiwari, "Upgradation of hemicellulose-derived furfuryl alcohol to butyl levulinate by using magnetic acidic deep eutectic solvents as catalysts," Catalysis Today, vol. 453, Mar. 2025, Art. no. 115276, doi: 10.1016/j.cattod.2025.115276.

4) The last scheme used alkaline DES as catalyst for aldolization of furfural with acetone. This is first instance in which basic DES was used as catalyst for aldolization of furfural. This paper is under preparation.

5**)** A comprehensive review on the use of DES in biomass valorization. This paper is under preparation.

Chemical Papers
https://doi.org/10.1007/s11696-024-03762-2

ORIGINAL PAPER

Esterification of lignin-derived phenolic compound eugenol to eugenol benzoate using acidic deep eutectic solvent as a catalyst

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Abstract
Eugenol is a lignin-derived aromatic model compound extracted from the lignin and has been used for various reactions. The eugenol esterification to eugenol benzoate with benzoic acid was studied using different deep eutectic solvents (DESs) as catalysts. DESs are a type of ionic liquid that is formed by combining a hydrogen bond donor with a hydrogen bond acceptor. In the current paper, carboxylic acids such as oxalic acid, acetic acid, p-toulenesulfonic acid (p-TSA) and tartaric acid were used as hydrogen bond donors to form choline-based DESs which were used as catalysts in esterification reactions. The catalysts were screened based on the conversion and p-TSA based DES was found to be best and used for further experiments. Effects of parameters (eugenol to benzoic acid ratio, reaction time, temperature, and catalyst loading) on the yield of eugenol benzoate were studied. The highest eugenol conversion was obtained as 90.42% (383 K, 0.02 g/cm^3 catalyst, molar ratio of eugenol to benzoic acid = 1:5, 600 rpm, 3 h).

Keywords Deep eutectic solvents · Eugenol benzoate · Acid catalyst · p-TSA-based DES · Lignin · Biomass

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Biobased synthesis of butyl levulinate from levulinic acid by using CTAB–based hydrophobic deep eutectic solvent as a catalyst

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Ravindra Joshi & Manishkumar S. Tiwari

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Abstract

The present research discusses the utilization of hydrophobic deep eutectic solvents (HDES) as acid catalysts in the green synthesis of n–butyl levulinate (BL) by esterification of levulinic acid (LA) obtained from cellulose. Butyl levulinate is used as a plasticizer, flavor, fragrance, solvent, and fuel additive. The HDES catalysts were synthesized from cetyl trimethyl ammonium bromide (CTAB) as hydrogen bond acceptor (HBA) and carboxylic acids (oxalic, citric, and para–toluenesulfonic acid monohydrate (p–TSAM)) as

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Upgradation of hemicellulose-derived furfuryl alcohol to butyl levulinate by using magnetic acidic deep eutectic solvents as catalysts

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ABSTRACT

In keeping with principles of green chemistry, the alcoholysis of hemicellulose-derived furfuryl alcohol (FAL) into butyl levulinate (BL) by using magnetic deep eutectic solvents (MDES) as catalysts were studied. This research is significant as it contributes to developing sustainable and environmentally friendly processes in the chemical industry. Butyl levulinate is emerging as a valuable fuel additive, and its synthesis through the furfuryl alcohol route is faster, cheaper, and environmentally benign. Deep eutectic solvents (DES) that possess magnetic susceptibility are called magnetic deep eutectic solvents. In the current research, H-bond donors used to synthesize MDES were various carboxylic acids such as citric acid, oxalic acid, and p-toluenesulfonic acid monohydrate (p-TSAM). Choline chloride was used as H-bond acceptor. Ferric chloride was added to impart magnetism. Among the three catalysts, p-TSAM-based MDES was found to be the most efficient and subjected to further optimization studies. Reaction parameters (mole ratio of FAL to n-butanol, time of reaction, temperature of reaction, and concentration of catalyst) were varied to maximize yield, and optimum values were found. The highest BL yield was 98.42 % (393 K, 0.02 g/cm^3 catalyst, molar ratio of FAL to n-butanol = 1:20, 600 rpm, 3 h). As the catalysts were magnetic, their isolation from the reaction mixture was unexacting. Catalyst recycling studies showed no appreciable loss of activity for four cycles.

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